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(54) Name of the invention: Surface Protective Film

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[Note : Names, addresses, Company names and brand names are translated in the most common manner. Japanese Language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.]

(54) [Name of the invention]

Surface Protective Film

(57) [Summary]

[Goal]

The goal of the present invention is to suggest a surface protective film with little plastic deformation at the time of the deformation, that has excellent stress relaxation properties, and elongation recovery properties, and also, that has little adhesion acceleration with the passing of the time.

[Structure]

Surface protective film, characterized by the fact that on one surface of a substrate material an adhesive agent layer is provided, and the substrate material is obtained as into polyolefin material with a crystallinity degree of 45 % or less, that is formed from ethylene - propylene copolymer and/or an alpha-olefin copolymer material, other than the ethylene - propylene, a plasticising agent with a molecular weight in the range of 300 ~ 1000, is added so that its amount is in the range of 3 ~ 30 weight %.

[Range of the claims of the invention]

[Claim 1]

Surface protective film, characterized by the fact that on one surface of a substrate material an adhesive agent layer is provided, and the substrate material is obtained as into polyolefin material with a crystallinity degree of 45 % or less, that is formed from ethylene - propylene copolymer and/or an

alpha-olefin copolymer material, other than the ethylene - propylene, a plasticising agent with a molecular weight in the range of 300 ~ 1000, is added so that its amount is in the range of 3 ~ 30 weight %.

[Detailed explanation of the invention]

[0001]

[Technological sphere of application]

The present invention is an invention about a surface protective film.

[0002]

[Previous technology]

Regarding the surface protective films, they have a structure where on one surface of a thermoplastic resin, etc., substrate material, an adhesive agent layer is provided, and they should have an appropriate degree of adhesive force (temporary adhesive properties) and together with that they should be materials whereby after the use, one part of the adhesive layer of the above described surface protective film is not separated and does not remain on the surface of the different types of materials that are subject to the adhesion, like synthetic resin plates, decorative plywood, metal plates, coated steel plates, etc., and also that the material that is contained in the adhesive layer is transferred and can be easily separated (released), and there is no staining of this front surface.

[0003]

Especially, there are cases where mechanical technological processes are conducted until the temporary adhesion of the above described surface protection film on the material that is the subject of the adhesion, however, in these cases, in addition to the originally required properties of the surface protective film, like the above described temporary adhesion properties and repeat release properties, it is also necessary that it is a material that is equipped with mechanical processing properties. Among the already existing substrate materials used in the surface protective films, the manufactured from soft vinyl chloride film, is the most preferred material, and because of that the surface protective films, that are obtained by using as the film material, material manufactured from a soft vinyl chloride resin that is formed by the calendering - forming (molding) method, the extrusion molding method, etc., and by providing an adhesive agent layer on one of its surfaces, have been widely used.

[0004]

However, in the case of the films manufactured from soft vinyl chloride resin, at the time of the waste incineration after the usage, there is a problem for the environment because of the generated hydrochloric gas, etc.. And because of that studies have been conducted for the advantageous use of films manufactured from olefin type resins that are relatively easy waste incineration treatment after the usage, as surface protective films instead of the above described films made from the soft vinyl chloride resin material.

[0005]

As the mechanical processing properties of the above described surface protective films, it is necessary to be a material that at the time of the mechanical processing changes its shape according to the deformation of the material on which it has been adhered occurring at the time of the mechanical processing. However, it is necessary that it is a material where there is no further deformation than that and there is no floating and separation from the surface of the material on which it is adhered, but also, it is necessary that it is a material where the above described load stress does not remain localized in the state as it is, but it is immediately relaxed, stated otherwise, it is a material that has little plastic deformation at the time of the deformation and that has excellent stress relaxation properties and elongation recovery properties.

[0006]

Regarding the mechanical processing properties of the above described surface protective film, mainly, the contribution of the properties of the substrate material layer is large, however, there is also a correlation with the adhesive force at the interface between the adhesive agent layer and the material that is being subjected to the adhesion. And if in order to prevent the separation of the surface protective film from the surface of the material on which it has been adhered, at the time of the mechanical processing, the adhesive strength of the adhesive agent layer is increased, the release of the surface protective film from the surface of the material that is the subject of the adhesion, becomes difficult, and the so-called adhesion acceleration properties become a problem.

[0007]

As experiments in order to improve the above described problem, for example, in the report of the description of the Japanese Patent Application Laid Open Number Showa 52-62347, the surface protective sheet has been disclosed that is manufactured according to the following: to the adhesive agent composition material, phosphoric acid ester or its derivative materials, are added so the added amount becomes more than 0.001 weight parts and

less than 0.5 weight parts, and the adhesive agent composition used in surface protective films, is coated on one of the surfaces of a polyethylene film, that has been subjected to a corona treatment, so that its thickness after drying becomes 10 microns, and then it is dried.

[0008]

However, in the case of the surface protective sheet that has been disclosed according to the above described Japanese Patent Application Laid Open Number Showa 52-62347, it is known that, depending on the type and the compounded amount of the used phosphoric acid esters or their derivative compounds, the adhesion acceleration properties, are improved. However, because there is no detailed description of the polyethylene film, if it is interpreted as being the usually used low density polyethylene film material, it is not a material that appropriately combines the above described mechanical processing properties.

[0009]

Also, in the report described according to the Japanese Patent Application Laid Open Number Showa 54-133577, the laminated layer film has been disclosed, that is a laminated layer film formed from polyethylene type resin layer and an adhesive resin layer, where the above described polyethylene type resin layer is formed from a composition obtained as relative to 100 weight parts of low density polyethylene, in the range of 3 ~ 60 weight parts of ethylene - vinyl acetate copolymer material, that contains 20 weight % or more of vinyl acetate, and in the range of 1 ~ 35 weight parts of plasticising agent, are compounded; and also, where the above described adhesive resin layer is an ethylene - unsaturated ester copolymer layer.

[0010]

However, in the case of the laminated layer film that has been disclosed according to the above described Japanese Patent Application Laid Open Number Showa 54-133577, there are no particular limitations relative to the low density polyethylene that is used in the polyethylene type resin layer, and any type of the usual, commercially available low density polyethylenes, can be used; and it is a material where to that ethylene - vinyl acetate copolymer that contains 20 weight % or more of vinyl acetate, is compounded, and because of that, the adhesive force occurring at the interface between the polyethylene type resin layer and the adhesive resin layer, is increased, and the adhesive force relative to the material on which this is adhered, is also increased, and with the passing of the time, the adhesion is accelerated, and after the usage, the separation of the surface protective film from the surface of the material, on which it has been adhered, becomes difficult. And also, it is not a material that corresponds to the requirements for the product, which

are that it be a material that has little plastic deformation at the time of the deformation during the mechanical processing, and that has high stress relaxation properties and elongation recovery properties.

[0011]

[Problems solved by the present invention]

The present invention is an invention that has taken into consideration the above described circumstances, and it is an invention that has as a goal to suggest a surface protective film with little plastic deformation at the time of the deformation, that has excellent stress relaxation properties, and elongation recovery properties, and also, that has little adhesion acceleration with the passing of the time.

[0012]

[Measures in order to solve the problems]

the present invention is an invention about the essential conditions for a surface protective film, characterized by the fact that on one surface of a substrate material an adhesive agent layer is provided, and the substrate material is obtained as into polyolefin material with a crystallinity degree of 45 % or less, that is formed from ethylene - propylene copolymer and/or an alpha-olefin copolymer material, other than the ethylene - propylene, a plasticising agent with a molecular weight in the range of 300 ~ 1000, is added so that its amount is in the range of 3 ~ 30 weight %.

[0013]

Regarding the used according to the present invention, polyolefin that has a degree of crystallinity of 45 degree or less, and that is used as the substrate material, it is a material that is formed from ethylene - propylene copolymer material and/or an alpha-olefin copolymer material other than ethylene - propylene. And as the above described alpha-olefin, for example, it is possible to use 1-butene, 1- hexene, 1 -octene, etc. In the case when the crystallinity degree of the above described polyolefin exceeds 45 %, it is not possible to obtain a substrate film that has little plastic deformation at the time of the deformation, and that has excellent stress relaxation properties and elongation recovery properties.

[0014]

Regarding the above described polyolefin that has a degree of crystallinity of 45 degree or less, and that is formed from ethylene - propylene copolymer material and/or an alpha-olefin copolymer material other than ethylene -

propylene, as long as it is a polymerization method where the crystallinity degree can be controlled at 45 % or less, it is possible to advantageously use any polymerization method. However, this material can be easily obtained by a copolymerization by the reactor blend method. Here, as the reactor blend method, it is a polymerization method where it is possible to manufacture such that the polymerization is not completed by one cycle, and a multistep polymerization of 2 and more steps is conducted, and by that, a number of different types of polymers are continuously manufactured. And it is a method where by using mechanical means, a mixed resin material from different types of polymers is obtained, and because of that it is a method that is completely different from the so-called, usual polymer blend method, and it is a method where a copolymerized resin material is produced that is a blended at a molecular level. Regarding the obtained by that polyolefin resin material, that has a crystallinity degree of 45 % or less, each of the different copolymerization components are finely dispersed and by that a mixed copolymerization component is obtained and provided, and a material is obtained where there is no expression of the properties of the different types of properties of the different materials, and it is a material that is a faithful embodiment of the mixed copolymer components. As detailed manufacturing methods, for example, there is the method that has been reported in the Japanese Patent Application Laid Open Hei-Sei 3-205439.

[0015]

There are no particular limitations regarding the above described plasticising agent that has a molecular weight in the range of 300 ~ 1000, and for example, it is possible to use the following here below materials: di - (2-ethylhexyl) phthalate, didecyl phthalate, etc., phthalic acid ester type plasticising agents, di - (2-ethylhexyl) adipate, didecyl adipate, etc., adipic acid ester type plasticising agents, di - (2-ethylhexyl) azelate, didecyl azelate, etc., azelaic acid ester type plasticising agents, di - (2-ethylhexyl) cebacate, didecyl cebacate, etc., cebacic acid ester type plasticising agents, 2-ethylhexyl oleate, etc., oleic acid ester type plasticising agents, trioctyl trimelitate, tetraoctyl pyromelitate, etc., trimelitic acid ester type plasticising agents, pyromelitic acid ester type plasticising agents, adipic acid ester, azelaic acid ester type plasticising agents, cebacic acid ester type etc., polyester type plasticising agents, chlorinated polyolefin type plasticising agents, etc.

[0016]

In the case when the molecular weight of the above described plasticising agent is less than 300, the above described plasticising agent that is present inside the substrate material layer, is transferred to a significant degree into the adhesive agent layer, and the adhesive performance is decreased and at the same time, the degree of staining of the material that is the subject of the adhesion, becomes high. And on the contrary, in the case when the

molecular weight exceeds 1000, the compatibility properties relative to the above described polyolefin material, are decreased, and a sufficient substrate material performance is not obtained, and besides that, the diffusion into the adhesive agent layer is hindered and the effect of the control of the adhesion acceleration, is not obtained to a sufficient degree, etc. And because of that, neither of these options are preferred options.

[0017]

Regarding the amount added from the above described plasticising agent that has a molecular weight that is in the range of 300 ~ 1000, it is in the range of 3 ~ 30 weight % relative to the above described polyolefin with a degree of crystallinity of 45 % or less. And in the case when the above described addition ratio is less than 3 weight %, the effect from the addition is not sufficiently demonstrated, and also, in the case when the amount added exceeds 30 weight %, the amount of the plasticising agent that is transferred to the adhesive agent layer, is increased, and the adhesive agent layer anchoring is decreased, etc., and because of that the adhesive properties are decreased, and at the same time, the degree of staining of the material that is the subject of the adhesion, becomes high.

[0018]

Moreover, in order to increase the practical use feasibility properties of the surface protective film, when a release agent is used on the back surface of the substrate material, and in the case of a soft substrate material, the front surface becomes difficult to slip, and because of that, it is possible that, in the part of the surface layer, another resin layer is laminated as laminated layer, and it is possible that in the raw materials that form the structure of the substrate material, other compounding materials are added, as long as it is in the range where it does not hinder the target results according to the present invention. For example, it is possible to add a filler agent, or a coloring agent, etc.

[0019]

In the case when by using the above described raw materials, the substrate material of the surface protective film according to the present invention, is obtained, as the thickness of this substrate material layer, although it varies depending on the thickness of the plate of the material that is appropriately used as the subject of the adhesion, usually, it is a thickness that is in the range of 30 ~ 100 microns. There are no particular limitations regarding the method for the preparation of the above described substrate material of the surface protective film, and for example, it is possible to use the extrusion molding method employing a T die or a circular die, a calendering forming method, a casting forming method, etc.

[0020]

Also, as the adhesive agent that is used in the surface protective film according to the present invention, there are no particular limitations, as long as it is a material that satisfies the performance as a surface protective film. And for example, it is possible to use a rubber type, an acrylic type, etc., adhesive agents. As the method for the formation of the above described adhesive agent layer, there are no particular limitations, and for example, it is possible to use the coating method, the co-extruding method, etc.

[0021]

[Effect]

Regarding the surface protective film according to the present invention, it is a surface protective film, where on one surface of a substrate material an adhesive agent layer is provided, and the substrate material is obtained as into polyolefin material with a crystallinity degree of 45 % or less, that is formed from ethylene - propylene copolymer and/or an alpha-olefin copolymer material, other than the ethylene - propylene, a plasticising agent with a molecular weight in the range of 300 ~ 1000, is added so that its amount is in the range of 3 ~ 30 weight %. And because of that, at the time when it is temporarily adhered as a surface protective film onto metal plates, etc., materials that are subjected to the adhesion, in the case when a bending technological process or a pressing technological process, etc., mechanical processing is conducted, at the time of the deformation, there is little plastic deformation, and it is also a material that has excellent stress relaxation properties, and elongation recovery properties, and also, that has little adhesion acceleration with the passing of the time.

[0022]

Regarding the effect of the surface protective film according to the present invention, as described here above, because of the fact that it uses polyolefin material, with a crystallinity degree of 45 % or less, that is formed from ethylene - propylene copolymer and/or an alpha-olefin copolymer material, other than the ethylene - propylene, the yield point strength is controlled to a low value, and appropriate elastic modulus is maintained. And by that, at the time of the mechanical processing of the material on which this has been adhered, it deforms in conformance to the deformation of the material on which it has been adhered, however, there is no deformation beyond that and floating and separation from the surface of the material that is the subject of the adhesion. And not only that, but also, it can be said that it is a material where the above described load stress does not remain localized in the state as it is, but it is immediately relaxed, stated otherwise, it is a material that has little plastic deformation at the time of the deformation and that has

excellent stress relaxation properties and embodies elongation recovery properties.

[0023]

Also, the plasticising agent molecules that are added within the above described range, are sustained in a relatively stable dispersed state in the non-crystalline (amorphous) part of the polyolefin molecules of the above described substrate material layer, and the preferred properties of the above described substrate material, are embodied. And in addition to that, at the time of the deformation that occurs during the above described mechanical processing, it is possible that an insignificant, but continual creep occurs, and the above described plasticising agent that is found at the interface with the material on which this surface protective film is adhered, provides also slipping properties, and altogether, it is concluded that it is a material that embodies excellent mechanical processing properties.

[0024]

[Practical Examples]

Here below, the present invention will be described in more details by using practical examples.

(Practical Example 1)

To 100 weight parts of ethylene - alpha-olefin copolymer material (trade name: Urutozex 1520, manufactured by Sanyo Petro-Chemical Company) 5 weight parts of dioctyl phthalate, are added, and by using the T-die method, a substrate material is manufactured with a thickness of 100 microns. On one surface of the above described substrate material, a corona electrical discharge treatment is conducted, and on this treated surface an acrylic type adhesive agent (trade name: AG 105, manufactured by Synthesis Research Chemical Company) is coated, so that after drying its layer thickness becomes 7 microns. And by that the surface protective film was manufactured.

[0025]

(Practical Example 2)

Instead of the used according to the procedures of the Practical Example 1, ethylene - alpha-olefin copolymer material, ethylene - propylene copolymer material (trade name: Hifax NKS021 P, manufactured by Himont Company) was used and everything else was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0026]

(Practical Example 3)

Instead of the 5 weight parts of dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 2, 10 weight parts of octyl trimelitate were used and everything else was conducted the same way as described in the technological procedures of the Practical Example 2, and by that the surface protective film, was manufactured.

[0027]

(Practical Example 4)

Instead of the 5 weight parts of dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 2, 5 weight parts of chlorinated paraffin were used and everything else was conducted the same way as described in the technological procedures of the Practical Example 2, and by that the surface protective film, was manufactured.

[0028]

(Reference Example 1)

To 100 weight parts of ethylene - alpha-olefin copolymer material (trade name: Urutozex 3520, manufactured by Sanyo Petro-Chemical Company), 10 weight parts of dioctyl phthalate, are added, and by using the T-die method, a substrate material is manufactured with a thickness of 100 microns. And everything else from here on was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0029]

(Reference Example 2)

The amount added of the dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 1, was changed to 50 weight parts, and everything else was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0030]

(Reference Example 3)

The amount added of the dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 1, was changed to 1 weight parts, and everything else was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0031]

(Reference Example 4)

Instead of the dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 1, 10 weight parts of dibutyl phthalate, were used and everything else was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0032]

(Reference Example 5)

Instead of the dioctyl phthalate plasticising agent used according to the procedures of the Practical Example 1, 10 weight parts of adipic acid type polyester plasticising agent with a molecular weight of 1000 or higher, were used and everything else was conducted the same way as described in the technological procedures of the Practical Example 1, and by that the surface protective film, was manufactured.

[0033]

For the surface protective films that have been obtained according to the above described Practical Examples and Reference Examples, the degree of crystallinity, the initial adhesive force, the release force after passing of time, the presence or absence of yield point at the time of the deformation, the coefficient of the elongation recovery, the coefficient of residual stress and together with that the bending processing properties and the staining properties relative to the material that is the subject to the adhesion, were tested and evaluated according to the described here below methods. The results from the evaluation are shown in Table 1.

[0034]

1. Degree of crystallinity of the film: The film obtained by the T die method is sampled prior to the conducting of the corona electrical discharge treatment, and the degree of crystallinity was measured by using the Differential Scanning Calorimetry method.

[0035]

2. Initial adhesive force: From the obtained surface protective film, a testing piece was cut with a width of 25 mm, and this was glued onto the surface of a stainless steel plate (trade name: SUS # 304 HL, manufactured by Nishin Steel Manufacturing Company) under an environment of 23°C x 65 % RH, and by using a 2 kg roller, and it was left to stay for 20 minutes; and after that, the 180 degree peel adhesion force occurring at a separation rate of 300 mm/min, was measured.

[0036]

3. Separation (peel) force after the passing of time: The same test piece with a width of 25 mm that has been used according to the described in the previous paragraph initial adhesion force test, was glued onto a stainless steel plate, and it was exposed to the outdoor conditions for a period of 1 month, and after that under an environment of 23°C x 65 % RH, the measurement of the 180 degree peel force, was conducted. Moreover, in the case of materials where the adhesion was poor and prior to the measurement, the surface protective film was separated, this was marked as "separated" in the table.

[0037]

4. Presence or absence of yield point at the time of the deformation: From the film obtained by using a T die, a test piece was cut with a length of 40 mm and a width of 10 mm, and this was extended at an extension rate of 200 mm/min, and the presence or absence of yield point at the time of the deformation, was confirmed. In the table, the materials were evaluated in three grades: the materials where an yield point was not observed, were denoted as: no; and in the case when an insignificant yield point was observed, it was denoted as: there is small yield point, and the materials that showed a yield point were designated as: yes.

[0038]

5. Elongation recovery coefficient: From the film that has been obtained by using a T die, an experimental piece with a width of 10 mm, was cut, and it was elongated by using a tensile testing equipment where the chuck was made to be 40 mm, and the extensional rate was 200 mm/min, and the tensile strength is left open immediately after the length has become 80 mm, and after the passing of 5 minutes, the length is measured, and from the 80 mm the measured length is subtracted, and it is divided by the original length of 40 mm, and this value expressed as percent, is shown in the table as the elongation recovery coefficient.

[0039]

6. Residual stress coefficient: The same way as in the case of the elongation recovery coefficient described in the paragraph here above, a test piece with a width of 10 mm is elongated by using a tensile testing equipment where the chuck was made to be 40 mm, and the extensional rate was 200 mm/min, and at the tensile strength at the time when the length has become 80 mm, it was left to stay for 5 minutes elongated at the same length, and the prorated value of the tensile strength after 5 minutes expressed in percent, is shown in the table as the residual stress coefficient.

[0040]

7. Bending processing properties: the obtained surface protective film is glued onto the above described stainless steel plate with a thickness of 1.5 mm, and by using a bender, a 90 degree bending processing was conducted, and the presence or absence of breakage of the film, and the presence or absence of floating and separation of the surface protective film, etc., is observed as the bending processing properties. Regarding the results from the observation, in the table they are presented according to the following: materials where even after the smoothly bending processing, there is a tight adhesion of the surface protective film: O, materials where there is a floatation and separation of the surface protective film: X, materials where there is a break of the film during the processing :"break".

[0041]

8. Properties of staining of the material subject of the adhesion: After the testing of the bending processing properties according to the above described paragraph the surface protective film is separated, and the state of the glue residue on the surface of the stainless steel plate that is the materials subject to the adhesion, is observed. The results from the observation are evaluated in 3 grades: there is no glue residue: no, materials where the amount of glue residue is insignificant: there is a small amount, materials where there is a prominent amount of glue residue: yes.

[0042]

[Table 1]

* The amount added of the plasticising agent is number of weight parts relative to 100 weight parts of the polyolefin material.

Headings of the table:

1. Practical Examples, 2. Reference Examples, 3. crystallinity degree of the film, 4. molecular weight of the plasticising agent, 5. added amount of plasticising agent (weight parts), 6. initial adhesive force (g/25 mm), 7. separation force after the passing of the time (g/25 mm), yield point at the time of the deformation, 9. elongation recovery coefficient (%), 10. residual stress coefficient (%), 11. bending processing properties, 12. properties for staining of the material subject to the adhesion, 13. no, 14. yes, 15. yes a small amount, 16. break, 17. separated.

[0043]

[Results from the present invention]

The surface protective film according to the present invention has the above described structure, and because of that, in the state when it is temporarily adhered as a surface protective film on a metal plate, etc., materials subject to the adhesion, it is a material that in the case when there is bending processing or pressing processing, etc., mechanical processing, at the time of the deformation, there is little plastic deformation, and it is a material, that has excellent stress relaxation properties, and elongation recovery properties, and also, that has little adhesion acceleration with the passing of the time.

Patent Assignee: Sekisui Chemical Industries Company

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〔表1〕

		フィルム 結晶化度 (%)	可塑剂 分子量	可塑剂添 加量※ (重量部)	初期粘着 力 (g/25mm)	経時後剥 離力 (g/25mm)	变形時 降伏点 8	伸長回 復率 (%)	応力残 存率 (%)	曲げ加 工性	被着体 汚染性
実 施 例	1	37	380	5	120	150	無	82	65	○	無
	2	36	390	10	100	125	無	80	40	○	無
	3	36	546	10	120	140	無	1383	42	○	無
	4	36	350	5	90	120	無	80	42	○	無
比 較 例	1	56	390	10	60	剥離	有	62	75	切れ	有
	2	30	390	50	20	剥離	無	78	62	×	有
	3	38	390	1	140	600	有	82	65	切れ	有
	4	37	278	10	100	80	微有	82	65	○	微有
	5	37	>1000	10	140	560	有	82	65	切れ	有

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